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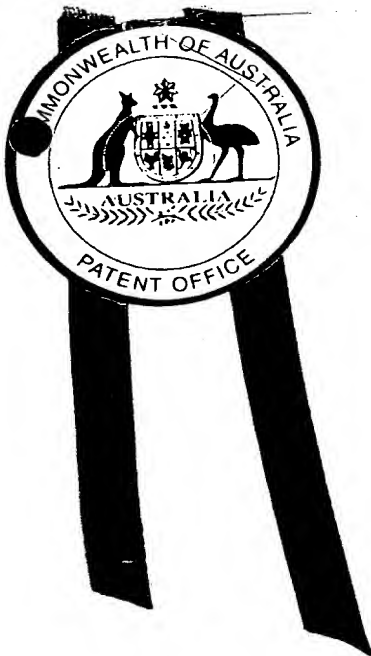
I, ANNA MAIJA MADL, ACTING TEAM LEADER EXAMINATION
SUPPORT & SALES hereby certify that annexed is a true copy of the
Provisional specification in connection with Application No. PQ 3413 for a
patent by VICTORIA UNIVERSITY OF TECHNOLOGY filed on
14 October 1999.

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A. M. Madl.

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PROVISIONAL SPECIFICATION

FOR THE INVENTION ENTITLED:

**"ERASABLE/REWRITABLE OPTICAL DATA STORAGE WITH
PHOTOREFRACTIVE POLYMERS USING CONTINUOUS WAVE
ILLUMINATION"**

Applicant:

VICTORIA UNIVERSITY OF AUSTRALIA

The invention is described in the following statement:

ERASABLE/REWRITABLE OPTICAL DATA STORAGE WITH
PHOTOREFRACTIVE POLYMERS USING CONTINUOUS
WAVE ILLUMINATION

This invention relates to optical data storage and more particularly to
5 erasable/rewritable three-dimensional optical data storage with photorefractive
polymers.

Multi-layered (or three-dimensional) optical memories have increasingly
become a field of interest in the development of high-density optical data storage
devices. Systems that utilise multiple layer recording can achieve recording
10 densities from 100 to 10,000 times higher than conventional optical data storage
devices.

The use of two-photon excitation in three-dimensional (3D) bit optical data
storage has grown due to its ability to increase the density in a given material by
reducing the volume of the recorded bit. The probability of two-photon excitation
15 is proportional to the squared intensity of the incident light; this effect produces
excitation only within a small region of the focus spot. As a result there is less
cross talk between neighbouring data layers. Another advantage of two-photon
excitation is the reduction of multiple scattering because of the utilisation of an
illumination beam of an infrared wavelength, so that more layers can be recorded
20 along the depth of a volume material.

Over the years different materials have been used for 3D bit data storage
under two-photon excitation. Two-photon 3D bits recorded in photopolymerizable
and photobleaching materials have demonstrated that recording densities could
reach terabits per cubic centimeter; unfortunately both materials are not erasable.
25 Photochromic materials that undergo a change in isomer states and photochromic
polymers that produce a change in refractive-index upon two-photon excitation are
both erasable materials. Another type of material that is of considerable interest is
photorefractive material. The photorefractive effect results in a modulation of the
refractive-index at the point of focus induced by the spatial distribution of electric
30 charges upon illumination.

It has been discovered that such a change in the refractive index in photorefractive material may be reversed by illuminating the medium again with radiation to produce a uniform redistribution of the electric charges and erase the recorded information. However, this has previously only been achieved in a
5 photorefractive crystals, e.g. lithium niobate (LiNbO_3), which are expensive to manufacture.

It is therefore desirable to provide a method of writing and erasing optical data in relatively inexpensive materials.

According to one aspect of the invention, there is provided a method of
10 writing and erasing optical data comprising:

producing a beam of focusable, coherent light;

focussing the beam on a photorefractive polymeric material to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to record data; and

15 illuminating the material with radiation to erase the recorded data.

According to another aspect of the invention there is provided a method of writing and re-writing optical data in a photorefractive polymeric material comprising:

focussing a beam of coherent light on the photorefractive polymeric material
20 to cause two-photon excitation of the material at the focal point of the beam thereby modulating the refractive index at the focal point to write data;

illuminating the material with radiation to erase the recorded data;

focussing another beam of coherent light on the photorefractive material to cause two-photon excitation of the material at the focal point of the beam thereby
25 modulating the refractive index at the focal point to re-write data in the photorefractive material.

Preferably, the photorefractive polymeric material used in the method is such that illumination with electro-magnetic radiation in the ultraviolet (UV) or visible spectrum produces a redistribution of the spacial distribution of the electric charges
30 forming the data bits to erase the recorded data. The photorefractive polymer is preferably arranged to absorb radiation in only a narrow band in the UV to visible

region of the electromagnetic spectrum. Creating a narrow absorption band will decrease the materials susceptibility to deterioration from the reading process or from incidental ultraviolet light (e.g. from sunlight).

Our Australian Provisional Patent Application No. PP8738 described the use
5 of a laser in a pulsed mode to write data by two-photon excitation of a photorefractive material. An ultrashort pulsed laser beam is typically used for two-photon excitation because the cooperative nature of two-photon excitation requires the use of a high peak power laser to produce efficient excitation. However, the use of an ultrashort pulse laser increases the cost of a recording device and makes it
10 difficult to produce a compact system. We have now demonstrated that two-photon excitation under continuous wave (CW) illumination is possible. Although the average power needed for CW excitation is increased by approximately two orders of magnitude compared with ultrashort pulsed illumination, the use of continuous wave illumination can enable a fast, low cost, compact erasable two-photon 3D bit
15 optical data storage system to be achieved.

The photorefractive material preferably includes a chromophore which provides absorption in the UV to visible region. The polymer may also be doped with a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum. In one embodiment, described in our
20 Australian Provisional Patent No. PP8738, the polymer comprises poly (N-vinylcarbazole) (PVK). In another preferred embodiment, the polymer comprises poly (methyl methacrylate) (PMMA). Each of these polymers may be doped with a photosensitive material, such as 2, 4, 7 - trinitro - 9 -fluorenone (TNF). One preferred chromophore is 2, 5 - dimethyl - 4 - (p - nitrophenylazo) anisole
25 (DMNPAA) which also provides absorption and an electro-optical effect in the UV to visible region. The polymeric material may also include a plasticiser, such as N-ethylcarbazole, (ECZ) to reduce the glass transition temperature of the material.

In the present invention, recorded bits of data may be read by employing a confocal microscope and/or a differential interference contrast (DIC) microscope
30 utilising a source of coherent light of a wavelength on the edge of or outside the absorption band of the photorefractive polymeric material.

According to a further aspect of the invention there is provided a photorefractive polymeric material for use in a method of erasable optical data storage, the photorefractive polymeric material providing absorption in the UV to visible region of the electromagnetic spectrum, wherein the absorption band of the photorefractive material is such as to enable the recording of bits of data by two photon excitation, the reading of the bits of data by a source of coherent light on the edge of or outside the absorption band, and the erasing of the bits of data by illumination with radiation within the absorption band. The polymeric material preferably comprises a polymer, such as PVK or PMMA. The material may include a chromophore which provides absorption in the UV to visible region of the electromagnetic spectrum. Optionally, the polymer may also be doped with a photosensitive material which provides absorption in the UV to visible region of the electromagnetic spectrum, and a plasticiser may be added to reduce the glass transition temperature of the material.

Preferably, a new photorefractive polymeric material in accordance with the second aspect of the invention includes at least some of the following materials in quantities falling substantially within the following ranges by percentage of the total weight of the photorefractive polymeric material:

- 25% - 100% of a polymer, such as PVK or PMMA;
- 0% - 60% of a chromophore, such as DMNPAA;
- 0% - 5% of a photosensitive material, such as TNF; and
- 0% - 40% of a plasticiser, such as ECZ.

A preferred embodiment of the present invention using a cheap photorefractive polymer as a recording material for rewritable/erasable 3D bit optical data storage under two-photon excitation to produce a high-density 3D optical data storage system will now be described by way of example only, with reference to the accompanying drawings, in which:-

Figure 1 is a graph showing the absorption curve of a photorefractive polymeric material for use in the present invention;

Figure 2 is a schematic diagram of a two-photon excitation microscope used to record and read 3D data bits in a photorefractive polymer;

Figure 3(a) is a bit pattern of the letter "E" recorded by two-photon excitation in a photorefractive polymer;

Figure 3(b) is the same region as Figure 3(a) after being exposed to UV illumination showing erasure of the recorded information;

Figure 3(c) is a bit pattern of the letter "F" written into the same area as Figures 1 and 2;

Figure 4 shows recorded bit patterns at different depths in the photorefractive polymer using two-photon excitation;

Figure 4(a) shows a first layer including letter "A";

Figure 4(b) shows a second layer including letter "B" and

Figure 4(c) shows a third layer including letter "C".

One example of a new photorefractive polymeric material that has been used to demonstrate rewritable/erasable 3D bit optical data storage is the polymer poly (methyl methacrylate) (PMMA) doped with the photosensitive material 2, 4, 7-trinitro-9-fluorenone (TNF) which provides absorption in the UV to visible region of the spectrum. The photorefractive material also included, as a chromophore, 2, 5-dimethyl-4-(*p*-nitrophenylazo)anisole (DMNPAA) which also provides absorption in the UV to visible region. In this experiment the randomly orientated chromophores were not aligned by applying an electric field (poling) during polymerisation and operation. Such a poling electric field is not necessary because the local electric field in the focus produced by a high numerical aperture objective is five orders of magnitude greater than that of the incident beam over the objective aperture. This local electric field is strong enough to induce a detectable electro-optic effect.

Finally *N*-ethylcarbazole (ECZ) was added to reduce the glass transition temperature of the material. One preferred concentration of the materials DMNPAA:PMMA:ECZ:TNF used was 10:73:16:1 by percentage weight of the total weight of the photorefractive material although it will be appreciated that different proportions of the constituent materials may be used within the ranges

specified above. Uniform films of thickness 100 μ m were fabricated by combining all the materials in a teflon cast then polymerising the PMMA at a temperature of 65°C over 2 days. The resulting polymer block was cut and polished to produce the sample used in the experiments.

5 Figure 1 illustrates the absorption band of a 100 μ m thick sample of the new photorefractive polymeric material as detected in an Oriel UV-Vis spectrophotometer using a Xenon arc lamp source.

It is seen from Figure 1 that the maximum of the absorption band of the new material is within 380-600 nm. Therefore a laser beam of an infrared wavelength at
10 800 nm can be used in the recording process to produce two-photon excitation at 400 nm. Since the absorption band cuts off approximately at a wavelength of 630 nm, a range of wavelengths from 630 nm to 750 nm can be chosen to read out the recorded photorefractive data bits without suffering from single-or two-photon excitation.

15 Referring to Figure 2, there is illustrated an optical system for two photon recording of bits of data and for reading the bits of data in the photorefractive polymeric material. The recording system comprises a laser (10), a mechanical shutter (11), linked to a computer (20), lenses (12, 13), a pin hole aperture (14), another aperture (16), and an objective lens (18). For reading with confocal
20 geometry, the system also includes a beam splitter (22), a further lens (24), another pin hole aperture (26) and a detector (28) also linked to the computer (20). A three-dimensional scanning stage (30) is provided for the mounting of the sample of photorefractive material (32). The scanning stage (30) is movable in the x, y and z directions under the control of the computer (20).

25 In the recording process, a Spectra-Physics Tsunami Ti:sapphire laser (10), operated in a continuous wave (CW) mode, was focused into the photorefractive polymer sample (32). Our Australian Provisional Patent Application No. PP8738 described use of such a laser in a pulsed mode. The wavelength of the laser was
30 tuned to 800 nm, which approximately corresponds to twice the wavelength of the main absorption band of the sample. From the absorption curve in Figure 1, we can see that there will be no single-photon absorption at a wavelength of 800 nm; only

the two-photon absorption can occur at a wavelength of 400 nm. The logic state of the recorded information was controlled by the mechanical shutter (11) linked to the computer (20). The recording material (32) was mounted upon a Melles Griot computer-controlled 3D translation stage (30). For recording an Olympus UPlanAPO objective (18) with a numerical aperture of 0.70 and a magnification factor of 20 was used.

For reading the change in refractive-index caused by the two-photon photorefractive effect an Olympus Fluo View microscope was employed and used in a differential interference contrast (DIC) mode. A He-Ne laser of wavelength 632.8 nm was coupled into the Fluo View for reading the recorded information, as the wavelength of 632.8 nm is on the edge of the absorption band and causes minimal damage to the recorded information (see Fig. 1). To erase the recorded information the region of interest was illuminated with either the UV line of the mercury lamp or in the Fluo View microscope. In both the reading and erasing an Olympus UPlanAPO objective (18) with a numerical aperture of 0.4 and a magnification factor of 10 was used.

Figure 3(a) shows the ability to record information as a change in refractive-index using continuous wave two-photon excitation. In recording an average power of 75 mW at the focus spot was used to record the information. A pattern (the letter E) consisting of 24 x 24 bits was recorded in the sample. The bit separation was 5.6 μm , and the exposure time for each bit was 2 ms. In the reading process a laser beam of power less than 5 mW was scanned across the sample to produce the DIC image. Figure 3(b) shows the same region as seen in Figure 3(a) after being exposed to the UV illumination for 1-2 seconds. The result shows the complete erasure of the previously recorded information. In Figure 3(c), a new pattern, the letter "F" is written into the same area as used in Figures 3(a) and 3(b). Two artifacts are marked with circles 1 and 2 in Figures 3(a), (b) and (c) showing that the same area was used to erase and rewrite information.

Figure 4 demonstrates the ability of this system to record and read changes in refractive-index of multiple layers of information. Three layers of information were recorded with a layer separation of 25 μm . Each layer consists of a pattern of 24 x

24 bits. The first layer, recorded near the surface contains a pattern of the letter "A". The second and third layers consist of the letters "B" and "C", respectively.

It will be seen from the above that the present invention provides an effective method of recording, reading, erasing and rewriting three dimensional data in ~~relatively inexpensive photorefractive polymeric materials using continuous wave~~ (CW) two-photon excitation to record and re-write the data and illumination with radiation in the UV or visible region of the electromagnetic radiation to erase the recorded data.

It will also be appreciated that various modifications, alterations and improvements may be made to the preferred embodiment described above without departing from the scope and spirit of the present invention. Such modifications or improvements that are envisaged to increase the storage capacity of the system include the following:

1. The compensation of small amounts of cross talk between the layers (see Figure 4) due to spherical aberration from the refractive-index mismatch between the recording material ($n = 1.75$) and the immersion medium ($n = 1$). The refractive-index mismatch results in an increase in the diffraction spot size at a deep position of a volume recording medium. As a result, a series of axial side peaks occur along the depth of the recording medium, thus resulting in cross talk between neighbouring data layers. It may be possible to overcome this problem thereby increasing the density of data by using a variable tube length method.

2. Instead of the Ti:sapphire laser operated in CW mode, other types of continuous wave (CW) laser beams may be used to produce the two-photon excitation. For example, with the help of a 1.2 W CW laser diode, operated at a near-infrared wavelength, a fast, low cost, compact, erasable two-photon 3D bit optical data storage system can be achieved.

3. Different photorefractive polymers may be used and the chemical properties of the materials may be modified to lead to an increase in the stability of the photorefractive polymer. By tailoring the absorption spectrum we can determine the wavelength of light that will affect the material. Creating a narrow absorption band in the UV or visible region will decrease the materials

susceptibility to deterioration due to irradiation from the reading process or from incidental UV light (i.e. sunlight).

4. A method for increasing the density of the two-photon data storage system by utilising a recording method may be based on the polarisation state of the recording beam. This technique allows multiple bits to be recorded at the same position within the material using different polarisation states of the recording beam, where upon reading, only the bits with the same polarisation state as the reading beam are detected.

5. A method for selective bit erasure in the two-photon data storage system may be based on polarisation of the recording and reading beams. An individual bit can be selected and erased by changing the polarisation state of the recorded bit, such that its polarisation state is different to that of the reading beam, and therefore not detected (erased).

DATED: 14 October 1999

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1/4

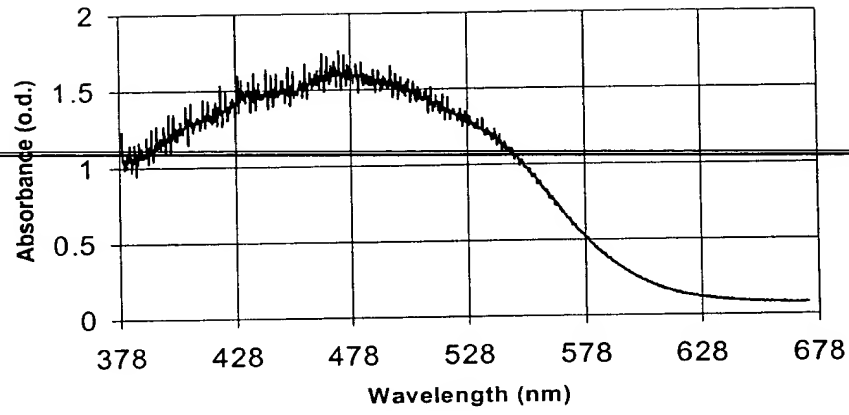


Figure 1.

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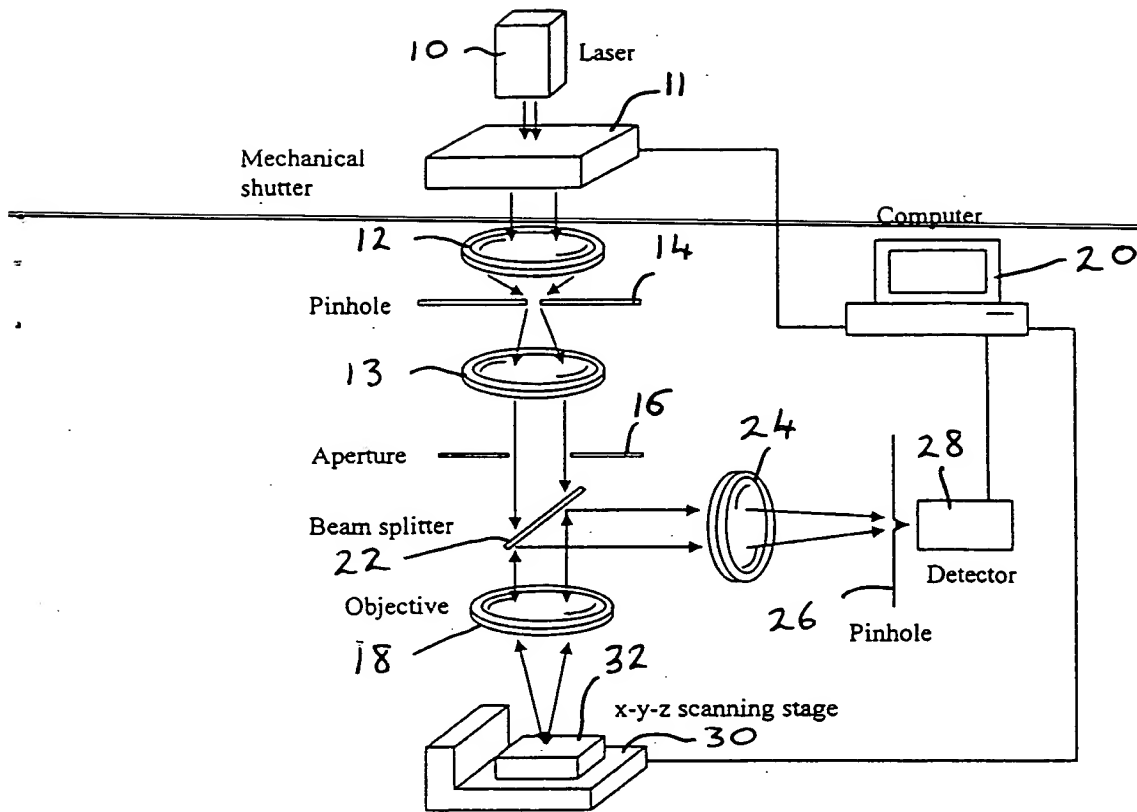
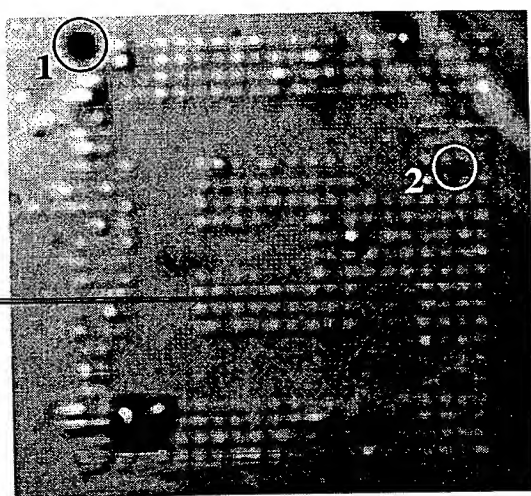
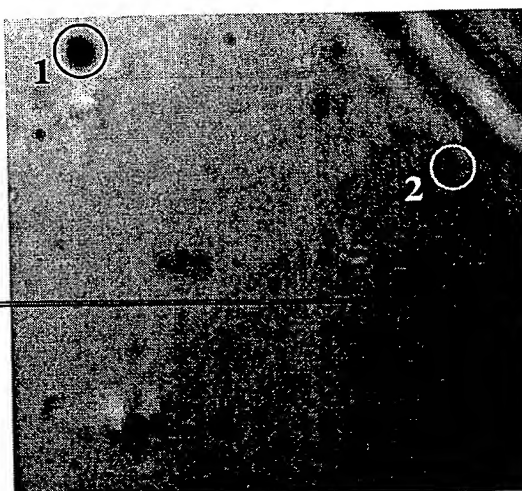


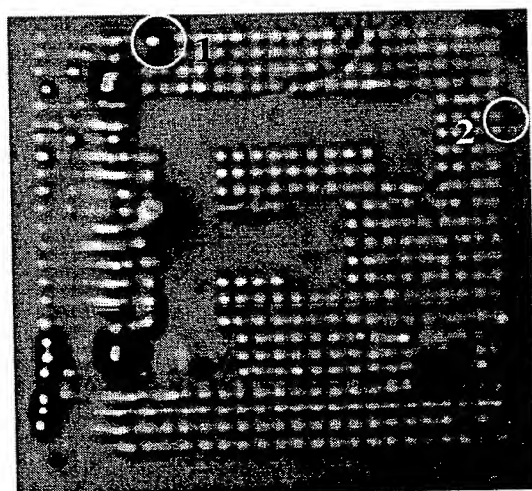
Figure 2.



(a)

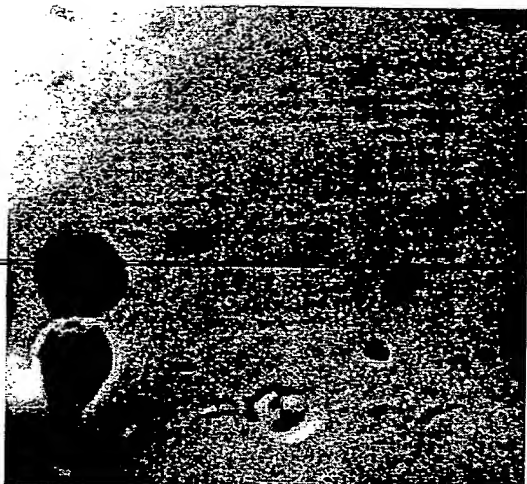


(b)

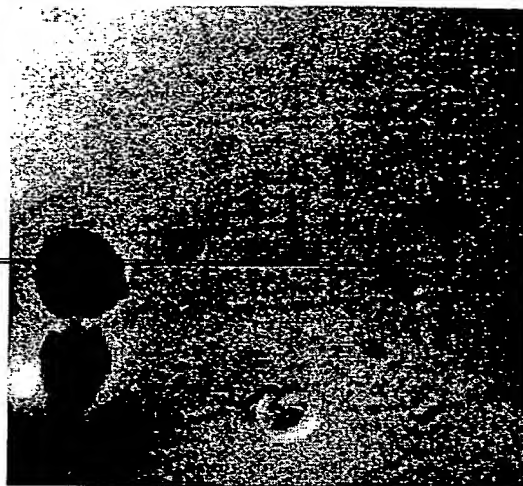


(c)

Figure 3.



(a)



(b)



(c)

Figure 4.

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